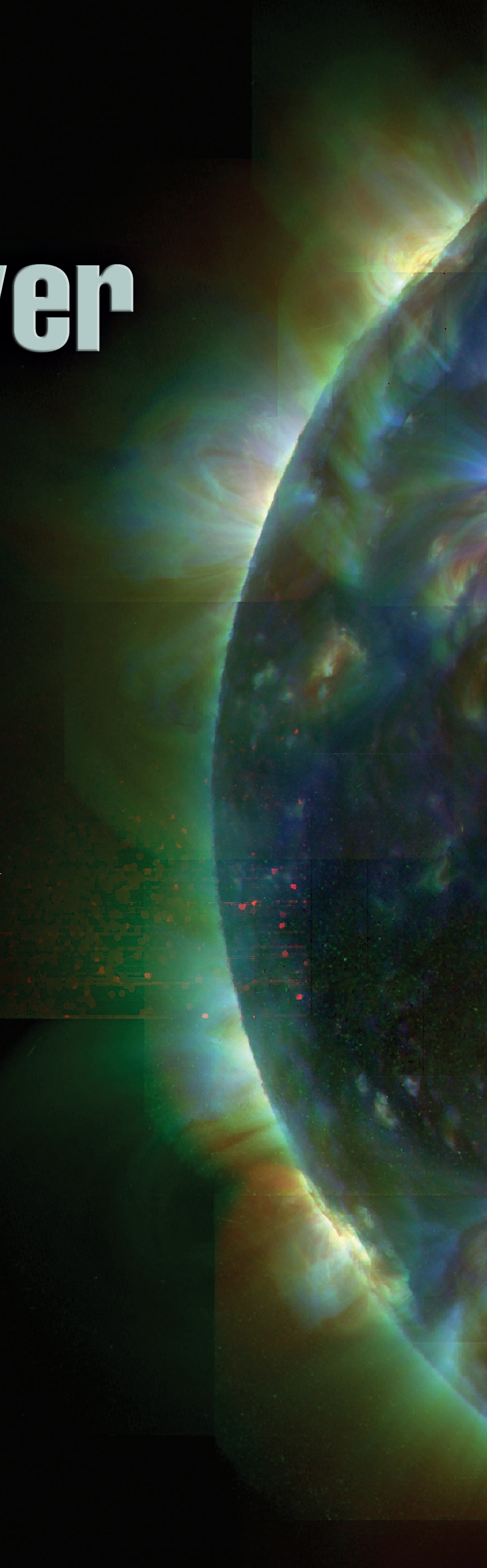
Atom by Atom, Layer by Layer



Thousands of atomically engineered layers add up to strong, wear-resistant, and even energetic materials.

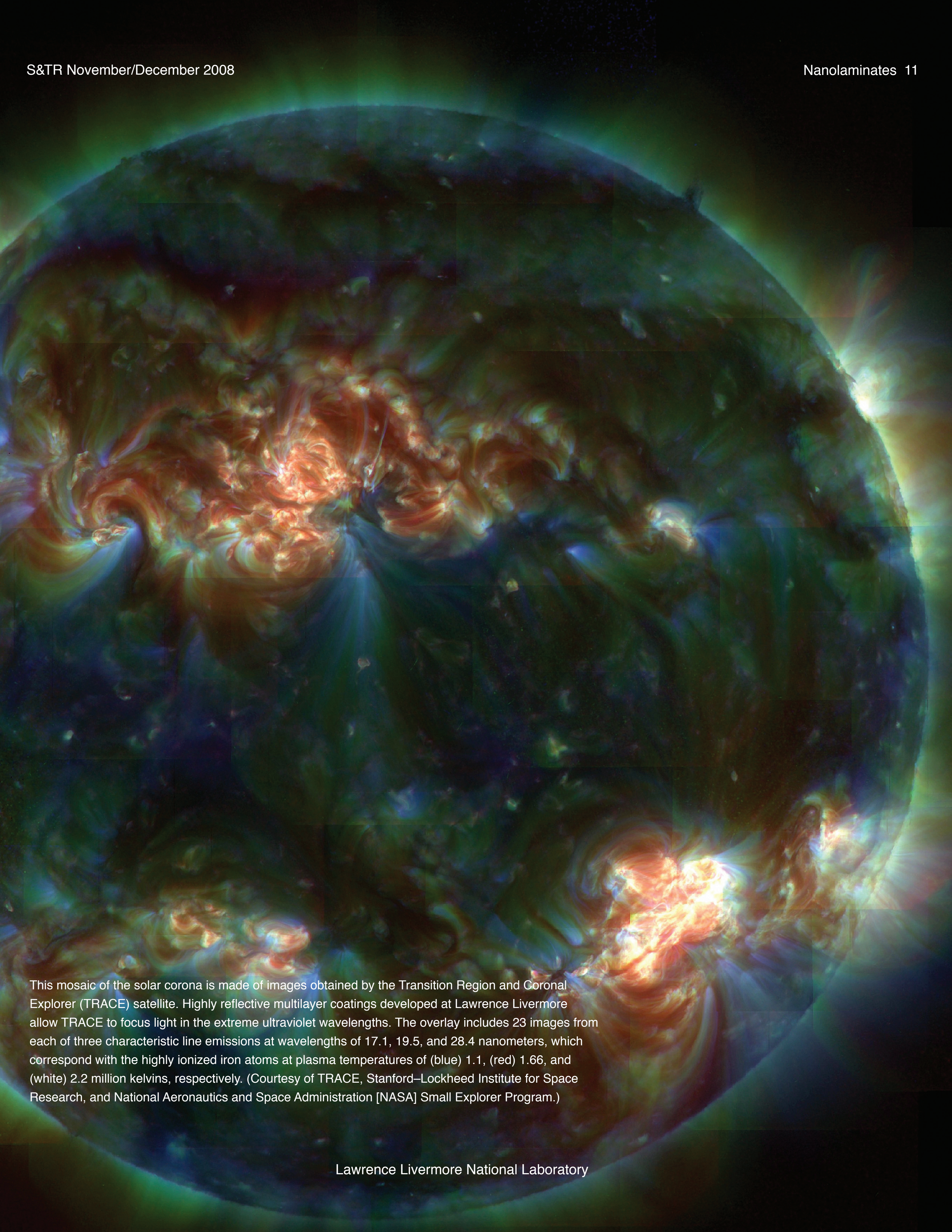
CALL them nanolaminates, or call them multilayers. In either case, they are atomic-scale sandwiches, composites made from dozens of alternating layers of materials, with each layer just 0.2 to 200 nanometers thick. The thickest layer may be only a few thousand atoms across, 1 one-hundredth the width of a human hair.

By carefully combining various elements and layer thicknesses, researchers can fabricate multilayers to almost any specification. These "designer" materials may be extremely strong; highly reflective; unusually ductile; or exceptionally resistant to heat, wear, and corrosion. Or they may incorporate several of those properties at the same time.

Many space-based solar astrophysics mirrors incorporate highly reflective multilayer coatings, allowing researchers to view the Sun's corona in the x-ray and extreme ultraviolet wavelengths. Another early use of multilayer synthesis technology was to manufacture magnetic hard-disk drives for computers. In this application, various metallic alloys are layered together with a magnetic layer on top for storing data. A more recent nanolaminate development—a layered foil that releases heat energy in a controlled manner—can be used to bond dissimilar materials without damaging them.

Most of these innovations are the brainchild of materials scientist Troy Barbee, who has been leading the Laboratory's multilayer effort since he arrived in 1985. Many of his successes received funding in the incubation stage from Livermore's Laboratory Directed Research and Development Program. Now 71, Barbee shows no sign of slowing and remains as creative as ever.

After receiving a Ph.D. in materials science engineering from Stanford University, Barbee was named Laboratory Director of the Stanford Center for Materials Research, where he performed



This mosaic of the solar corona is made of images obtained by the Transition Region and Coronal Explorer (TRACE) satellite. Highly reflective multilayer coatings developed at Lawrence Livermore allow TRACE to focus light in the extreme ultraviolet wavelengths. The overlay includes 23 images from each of three characteristic line emissions at wavelengths of 17.1, 19.5, and 28.4 nanometers, which correspond with the highly ionized iron atoms at plasma temperatures of (blue) 1.1, (red) 1.66, and (white) 2.2 million kelvins, respectively. (Courtesy of TRACE, Stanford–Lockheed Institute for Space Research, and National Aeronautics and Space Administration [NASA] Small Explorer Program.)

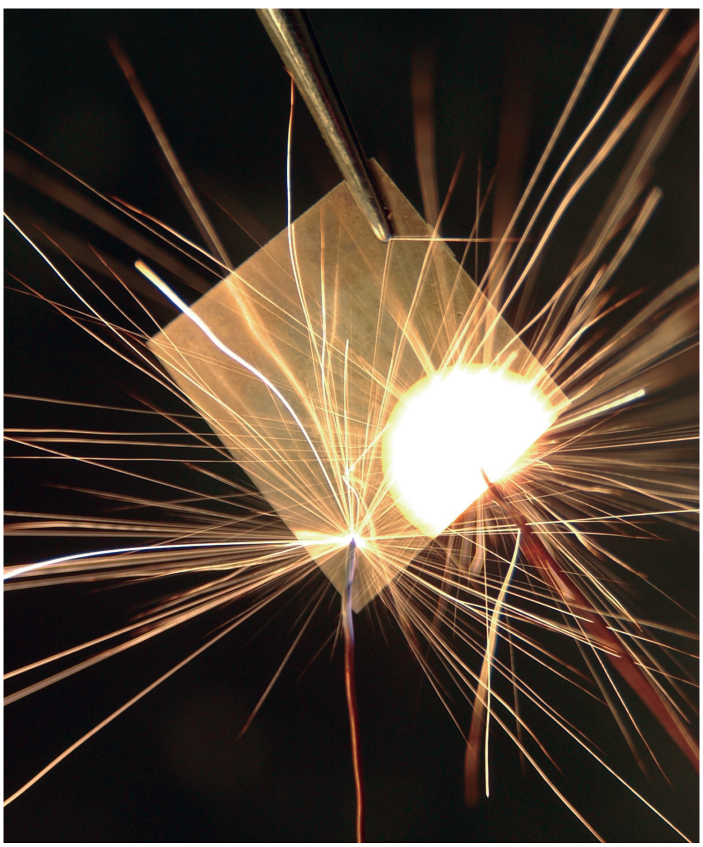
some of the earliest work with atomically engineered multilayers. Barbee notes that multilayer technology proved so successful in magnetic memory hard drives, technologists put it to use before anyone thought to patent it.

Atomic engineering does not rely on thermodynamics and kinetics to create new or advanced materials. Fabricating nanolaminates using atom-by-atom sputter deposition transcends the limits of standard manufacturing methods, resulting in materials with surprising properties, always different from those of the component substances in bulk form. These properties are due to the nanometer-scale environment of the atoms in each layer. Layers range from several atoms to a few thousand atoms thick, and the atoms within a layer are strongly influenced by the interfaces between the component layers.

Finding applications for these unusual materials is one part of the fun for Barbee, who works in Livermore's Physical and Life Sciences Directorate. "I get great enjoyment from seeing these creations put to work," he says. "So I have always emphasized working with collaborators and finding uses for our new multilayers."

Collaborations with the National Aeronautics and Space Administration (NASA) and various branches of the U.S. government put multilayered telescope mirrors and other optical devices into space. Working with Pratt & Whitney, researchers developed refractory oxide nanolaminates to enhance the performance of aircraft turbine blades. That cooperative effort produced the technology now used to fabricate high-energy-density electrical capacitors. Livermore nanolaminates also make possible extreme ultraviolet lithography (EUVL), a new lithographic method for cramming more devices onto a silicon chip.

Companies have worked with the Laboratory to determine whether the reactive nanolaminates can deploy automobile air bags or deliver inhaled medications. Government agencies have discussed using a reactive nanolaminate as an anti-tamper device on a weapon or other high-value item. And the list goes on.



The reactive nanolaminate commercialized by Reactive NanoTechnologies, Inc., is a new tool for soldering. In the reaction area (white), the temperature has jumped to 1,500°C, while the remainder of the foil is still at room temperature. (Courtesy of Reactive NanoTechnologies, Inc.)

The Shortest Wavelengths

While at the Stanford Center for Materials Research, Barbee developed the process for fabricating fully dense thin films using the then-new magnetron sputter sources. With these materials, he could study the mechanical properties at the size limits of microstructure control. In fact, the results opened the scientific door to a new world of atomic engineering and designer materials. (See the box on p. 13.)

"A combination of tungsten and carbon layers turned out to demonstrate the optical quality needed for x-ray optics," says Barbee. That finding led to the NASA collaboration to design multilayer coatings for telescope mirrors. Eventually, the coatings enabled the mirrors to focus light from space not only in the x-ray wavelengths but also in the extreme ultraviolet wavelengths. Livermore multilayer coatings are on the mirrors of NASA's Transition Region and Coronal Explorer (TRACE) satellite, which orbits Earth, pointing constantly at the Sun. Launched in 1998, TRACE records images and other data about the Sun's fluctuating magnetic fields, which cause sunspots, the corona, and other plasma structures. TRACE has vastly increased knowledge of the physics of sunspots and the Sun's corona.

A seemingly unrelated payoff to the successful use of multilayers in solar astrophysics was for computer chip manufacturing. Multilayer mirror coatings of molybdenum and silicon are a key technology for EUVL, a manufacturing technique that uses extremely short wavelengths of light to "write" on computer chips. EUVL will increase computer performance by shrinking the features printed on chips, thus allowing manufacturers to develop even smaller chips. Livermore is collaborating with other national laboratories and industrial partners to develop EUVL for commercial applications. (See *S&TR*, September/October 2008, pp. 21–23.)

Unusual Ductility

Barbee discovered an unusually ductile, high-strength nanolaminate by layering copper (Cu) with an alloy of copper and zirconium (CuZr). The Cu layer is nanocrystalline, with carefully ordered atoms in fine grains only a few atoms across. The atoms in the alloy layer have no order, resulting in an amorphous solid, similar to common window glass. Zirconium, often used in alloys, is soft, malleable, and highly resistant to corrosion. The Cu–CuZr laminate possesses significantly higher tensile strength than nanocrystalline copper. The thin, amorphous, atomically engineered metallic glass layers are highly ductile and plastic, deforming in conformity with the thicker copper layers and stretching considerably without fracturing.

Bulk metallic glasses such as window glass are brittle at room temperature. Likewise, most nanoscale microstructural materials easily crack under stress. Since the discovery of the highly ductile nanolaminate, various team members have explored the mechanical properties of this unusual material.

Using transmission electron microscopy (TEM) and subjecting a sample to various tensile strains, scientists can "watch" the microstructures change and see where dislocations and voids between grains of materials appear in the Cu–CuZr. Today, materials scientist Morris Wang, also of the Physical and Life Sciences Directorate, is collaborating with Barbee to determine why Cu–CuZr is so ductile. This past summer, *Nanotech Briefs* honored Wang with a 2008 Nano 50 Award for his work, part of which is with nanolaminates. The annual competition, held for the first time in 2005, recognizes the top 50 technologies, products, and innovators that have significantly advanced nanotechnology.

In the Cu–CuZr research, Wang tested amorphous layers ranging from 3 to 15 nanometers thick, with crystalline layers from 5 to 100 nanometers thick. Wang and Barbee's results, combined with molecular dynamics simulations by Ju Li of Ohio State University, indicate that the interfaces between the many layers are the key to the material's unusual ductility. Dislocations start at one interface, travel across a crystalline copper layer, and are absorbed at the next interface. TEM experiments also revealed that the tensile elongation occurs earlier in the amorphous CuZr at lower stress levels than in crystalline–crystalline multilayers. The interfaces are again critical for absorbing the dislocations, with all amorphous layers remaining intact during stress and strain tests.

A New Way to Join

A different collection of nanolaminate materials is helping things to explode in small ways—to fuse materials together—and in large ways—to detonate nonnuclear, conventional weapons. These nanolaminates, called energetic

Building a Better Nanolaminate

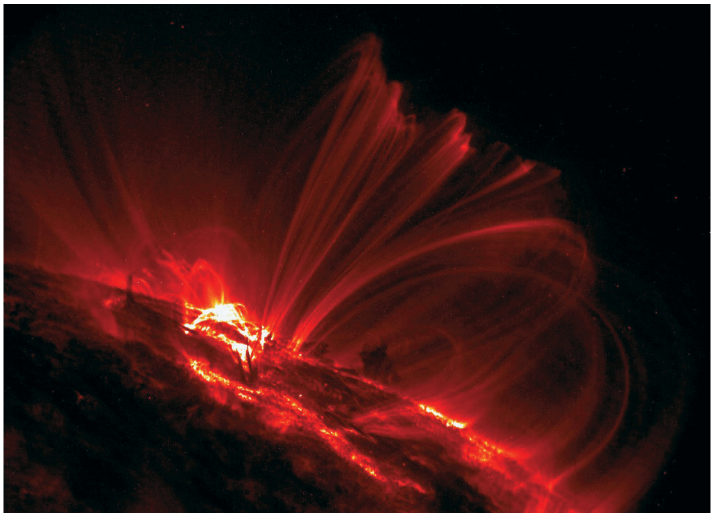
A multilayer, or nanolaminate, is a dense, ultrafine-grained solid composed of thousands of nanometer-scale layers. Each layer's thickness, composition, and structure are carefully controlled. On a substrate, such as silicon dioxide, the layers are laid down in a vacuum, leaving no opportunity for surface oxidation.

A multilayer product is typically synthesized using atom-by-atom processes such as molecular beam epitaxy, thermal physical evaporation, sputter deposition, chemical vapor deposition, and electrochemical technologies. The overall scale of the finished nanolaminate is determined during synthesis by controlling the thickness of the individual layers.

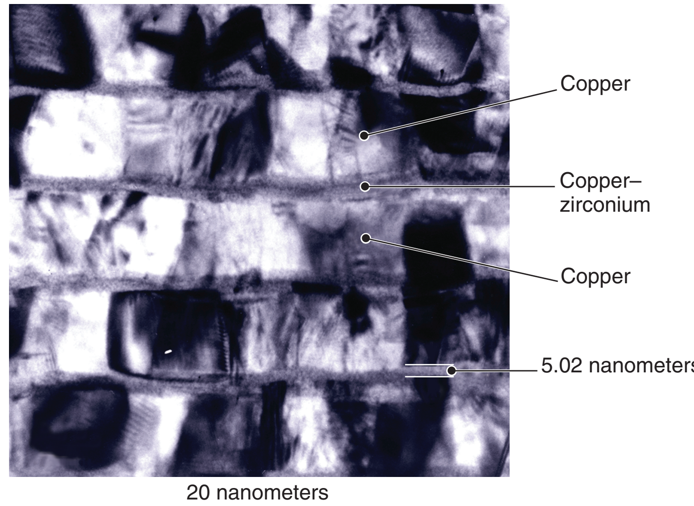
Livermore's primary method of building a nanolaminate is magnetron sputtering, a process developed by Laboratory materials scientist Troy Barbee for nanolaminate synthesis. In magnetron sputtering, a material is bombarded with electrically charged particles. Some of the material's atoms are knocked loose and travel to the item being coated, where atomic bonding forms a stable coating. Nanolaminates may have only 2 layers or as many as 200,000. Barbee, who leads the Laboratory's multilayer effort, says his team has synthesized nanolaminates from 80 of the 92 naturally occurring elements in elemental form, as alloys, or as compounds.

According to Livermore physicist Chris Walton, magnetron sputtering works extremely well, but it is slow and expensive. At the industrial level, large-scale roll coaters can be used for some nanolaminate applications, such as antireflective coatings and metallization. The high cost of most nanolaminates limits their use to critical, high-end applications or to small parts.

Walton leads a team that is modeling magnetron sputter deposition in support of Livermore's programmatic research. "We need to get on top of the physics," he says. The goal is to develop more precise models about crucial physical processes, which could be used to optimize the sputtering process. Faster deposition and lower costs would benefit all thin-film development efforts.



TRACE is acquiring data for research on the Sun's corona and other plasma formations. (Courtesy of TRACE, Stanford–Lockheed Institute for Space Research, and NASA Small Explorer Program.)



An unusually ductile nanolaminate is made by layering crystalline copper and the amorphous, unordered material copper–zirconium.

materials, store chemical energy in the same manner as rocket fuel, explosives of all kinds, and pyrotechnic products. Two or more nonexplosive solid materials are combined in layered form, remaining inert until activated by a mechanical thump, an electrical zap, or a scratch of friction.

Barbee and his postdoctoral researcher Timothy Weihs addressed the question of how or why energetic nanolaminates have such unique properties. As a result of their broad-ranging, systematic experiments, they developed a substantial advance in understanding the relationship between nanolayering and energetic response. Their research showed that materials in nanometer form, layered or not, would have this energetic property. Inherent in this understanding is the ability to relate the amount of stored potential energy, the scale of the material, and the rate of reaction and energy release in a quantitative, though parametric manner.

Weihs has since joined the faculty of Johns Hopkins University. In 2001, he and another Johns Hopkins faculty member founded Reactive NanoTechnologies, Inc., (RNT) in Hunts Valley, Maryland. Barbee and RNT won an R&D 100 Award in 2005 for NanoFoil®, the patented reactive nanolaminate developed in the Livermore–RNT collaboration. The same year, RNT received a Nano 50 Award for the material.

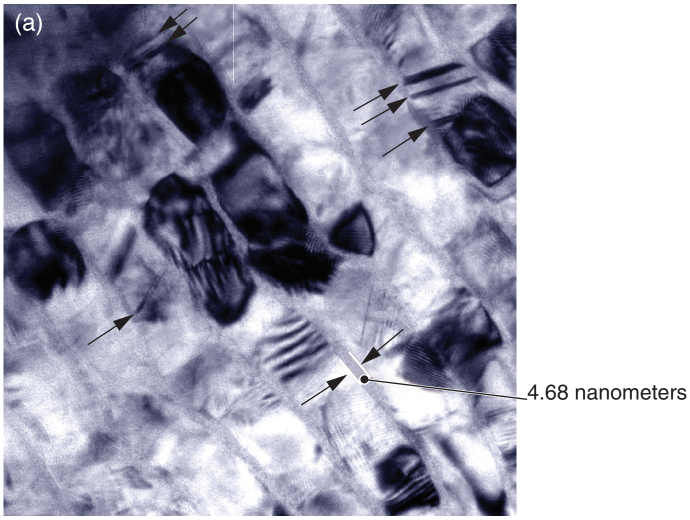
NanoFoil can be used to bond metals, ceramics, semiconductors, and polymers. It can replace lead-based soldering, which causes collateral damage to parts and is potentially toxic, and epoxies, which tend to degrade over time. With NanoFoil, a heat sink can easily be attached directly to a computer chip to conduct heat away from the chip.

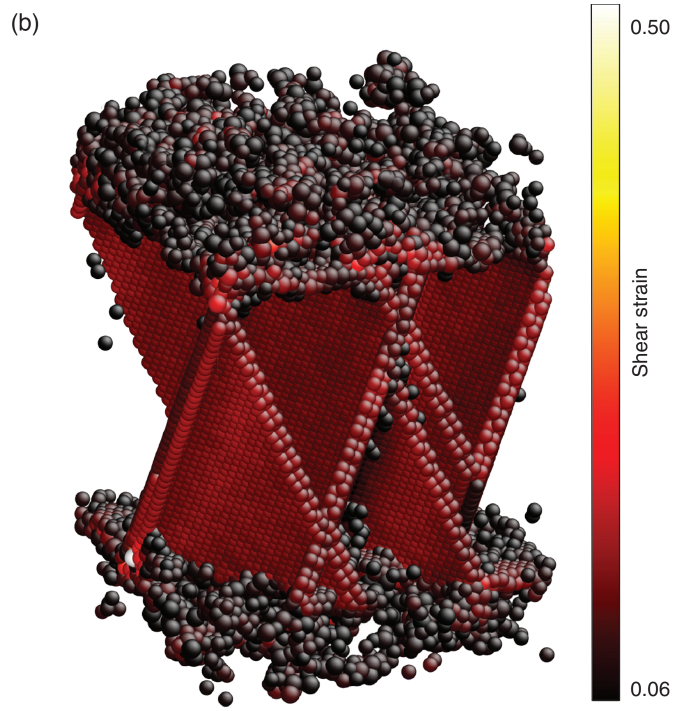
Today, RNT is bonding sputtering targets for companies that manufacture integrated circuitry, data storage devices, photovoltaic cells, and flat-panel displays. Says Weihs, "Since we make the bonding foil by sputtering, it's an interesting twist."

Packing Heat

Reactive nanolaminates are also being used in new warfare technologies. For example, RNT and Livermore worked with the U.S. military to develop materials that burn with the same heat signature as helicopters, which fly close to the ground and are often in harm's way. A nanolaminate decoy could distract a heat-seeking missile and save the helicopter and its occupants. The lightweight decoy would flutter in the air, staying aloft for a time rather than immediately plummeting to Earth.

In a detonator project, a Livermore team proposed using nanolaminate materials for the U.S. Strategic Environmental Research and Development Program, which is managed jointly by the Departments of Energy and Defense and the Environmental Protection Agency. "The project was part of the government's goal to 'green' the arsenal," says Laboratory chemist Alex Gash. In addition to Barbee and Gash, the Livermore team included solgel expert Joe Satcher from the Physical and Life Sciences Directorate and Randy Simpson, who along with Gash works in the Laboratory's Energetic Materials Center. The center conducts research on the performance of high explosives not only for the nuclear weapons program but also for advanced conventional weapons, rocket and gun propellants, homeland security,





(a) Under increasing strains, the Cu–CuZr nanolaminate shows streaks where deformation has occurred in the nanocrystalline copper layers. Despite the strain, the overall structure demonstrates its ductility by remaining intact. (b) Modeling reveals the sliding that occurs across the amorphous layers, which keeps the structure intact under strain.

demilitarization, and industrial uses of energetic materials.

The team's objective was to develop an environmentally safe stab detonator for medium-caliber (20- to 60-millimeter) munitions. Stab detonators, which are activated by a mechanical stimulus, ignite to detonate the main charge. The primer mix in conventional stab detonators contains two forms of lead and other highly toxic substances that pose a danger during manufacture and after detonation. In addition, some primer constituents are no longer made, so substitutes are needed.

The Livermore team developed an energetic nickel–aluminum nanolaminate that serves as the mechanically sensitive igniter for the energetic explosives in conventional munitions. Sensitivity can be enhanced with an energetic nanolaminate, which is environmentally safe yet fully functional as an igniter.

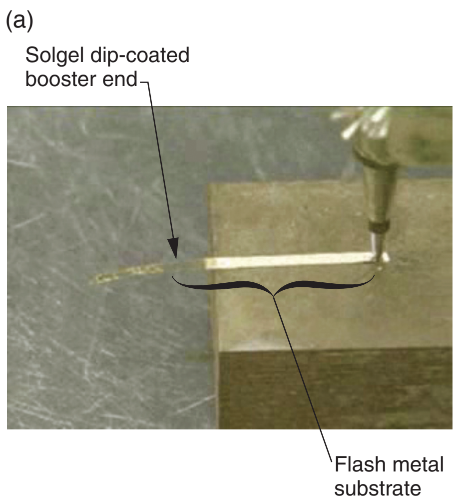
"By varying the layer thickness, we can modify the ignition sensitivity and the reaction speed," says Gash. A slower reaction could be used in a delay mechanism, similar to the device that keeps a parachute closed until a pilot is ejected from a plane. Specialized reactive nanolaminates with a delay mechanism may someday be used in commercial technologies, but at this time, the materials are too expensive for widespread application.

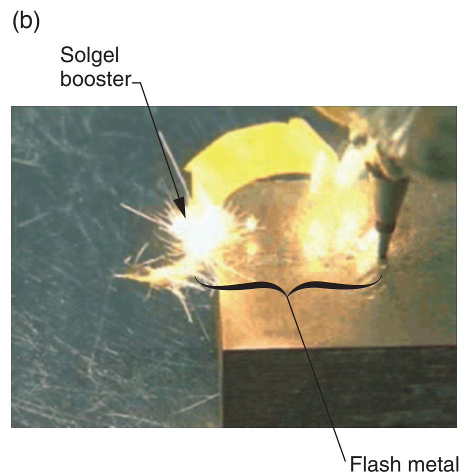
"Most energetic nanocomposites are powders whose combustion is difficult to control," says Gash, who also received a 2008 Nano 50 Award. In addition, most energetic nanocomposites do not age well because they are made of materials that readily oxidize in air. "With nanolaminates, the layers are self-contained, so they aren't as exposed to oxygen in the air," says Gash. "These materials also allow us to control the total energy output as well as the ignition conditions." Controlling the reaction is easily achieved by manufacturing the multilayer with specific layer thicknesses.

Barbee and others have explored many combinations of common elements for various weapons-related projects. For example, hafnium or zirconium layered with carbon may produce reaction temperatures well above 3,000 kelvins, perhaps even reaching 4,100 kelvins. "For all we know about nanolaminates, there is still a lot we don't understand," says Barbee. "Our experience in nanolaminate research has taught us to expect the unexpected."

Storing Energy

Livermore's Industrial Partnerships Office is marketing a commercial license for a nanolaminate fabrication process that can be used to create high-performance dielectric layers. With the Laboratory's Gary Johnson and Andrew Wagner, who is now at PPG Industries' Glass Technology Center, Barbee maximized the energy storage of the capacitor's dielectric layer while minimizing the capacitor's size. The team received initial funding from the U.S. government-sponsored Partnership for a New Generation of Vehicles. "The idea then was to use the capacitor in electric cars," says Barbee. Later, the Departments





In one Livermore project, researchers replaced the toxic materials typically found in the primers of munitions igniters with an environmentally friendly solgel material. (a) A nickel–aluminum reactive nanolaminate is dip-coated with the solgel booster. (b) A light spring-loaded punch activates the nickel–aluminum reaction, which in turn ignites the solgel booster.

of Energy and Defense funded research to adapt the capacitors for added reliability to nuclear weapons in the stockpile.

The prototype capacitor is 4 centimeters square and 1 millimeter thick and packs 50 joules per cubic centimeter of dielectric energy density. The goal is to develop a device no more than 1 centimeter on a side and half as thick as the prototype. These miniature capacitors could be used in power electronics control circuitry, automotive control systems, telecommunications, computers, radar systems, and other pulsed radio-frequency applications.

"Thirty years ago, the first nanolaminate pair I fabricated, niobium–copper, was designed for studying physical properties," says Barbee. "Today, that same material is being tested at Los Alamos [National Laboratory] as a radiation-damage-resistant material for use in future nuclear and fusion energy systems."

Who knows where a Livermore nanolaminate might turn up next. "Troy is amazing," says Weihs. "He just keeps going and going with lots of great ideas. In fact, I'd say he has more ideas than he can handle."

—*Katie Walter*

Key Words: energetic materials, extreme ultraviolet lithography (EUVL), magnetron sputter deposition, multilayers, nanolaminates, reactive materials.

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